EXPERIMENTAL INVESTIGATION OF CALCIUM MINERALS IN A VENUS SIMULATED ENVIRONMENT

S. T. Port[1], A. R. Santos[2], T. Kremic[1], G. W. Hunter[1]

[1]NASA Glenn Research Center, 21000 Brookpark Road, Cleveland, OH 44135, [2]Department of Earth and Environmental Sciences, Wesleyan University, Middletown, CT 06459

NASA POSTDOCTORAL PROGRAM

Introduction

- Venus' surface is ~460°C and ~95 bar with trace abundances (120-180 ppmv) of SO_2 [1]
  - SO_2 is reactive with several common elements including calcium [2-5]
- Knowledge on chemical reactions has implications for the past and current state of Venus
  - Venus may have had liquid water on its surface [6], thus hydrous silicates may have formed at that time [7].
    - To determine if these minerals are still present, tremolite and phlogopite were tested at simulated Venus conditions [7-8]
    - Conclusion:
      - They will be stable over billions of years and may still be present [7-8]
      - However, experiments were not completed in SO_2
  - The Venus Emissivity Mapper (on VERITAS and EnVision) will be used to determine bulk composition of the surface by observing transition metal content [9-10]
    - Calcium diffuses through basalt to react with CO_2 and SO_2, changing the bulk composition and decreasing the emissivity from orbit [9]
    - Experiments investigating kinetics will be informative for future emissivity data
- **Goal**:
  - Constrain reaction rate between several calcium minerals and SO_2
  - Determine the effect, if any, crystal lattices may have on these rates

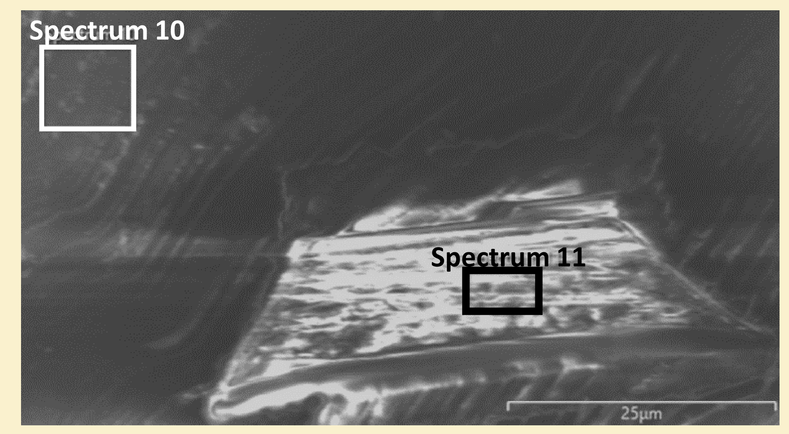
Methods

- Sample
  - Calcite ($CaCO_3$) was first because of its reactivity with SO_2 [2,8]
  - Polished then cleaned in an ultrasonic bath
  - Wrapped with gold wire
- Experiment
  - Sample is hung in the center of ceramic tube in TGA which completes Thermogravimetric Analysis (Figure 1)
  - Tested Gas:
    - CO_2/1.5% SO_2: SO_2 abundance similar to molecular number density as on Venus [2]
  - Tested Temperatures:
    - 460°C: average lowland temperature on Venus [1]
    - 700°C: to increase reaction rate
  - Temperature and mass of sample are collected in real-time
- Analysis
  - Milled using a Focused Ion Beam (FIB)
  - Analyzed with Scanning Electron Microscope/Energy Dispersive X-Ray Spectroscopy (SEM/EDS)

Figure 1: Experimental Apparatus used in these experiments.

Results

460°C Experiment



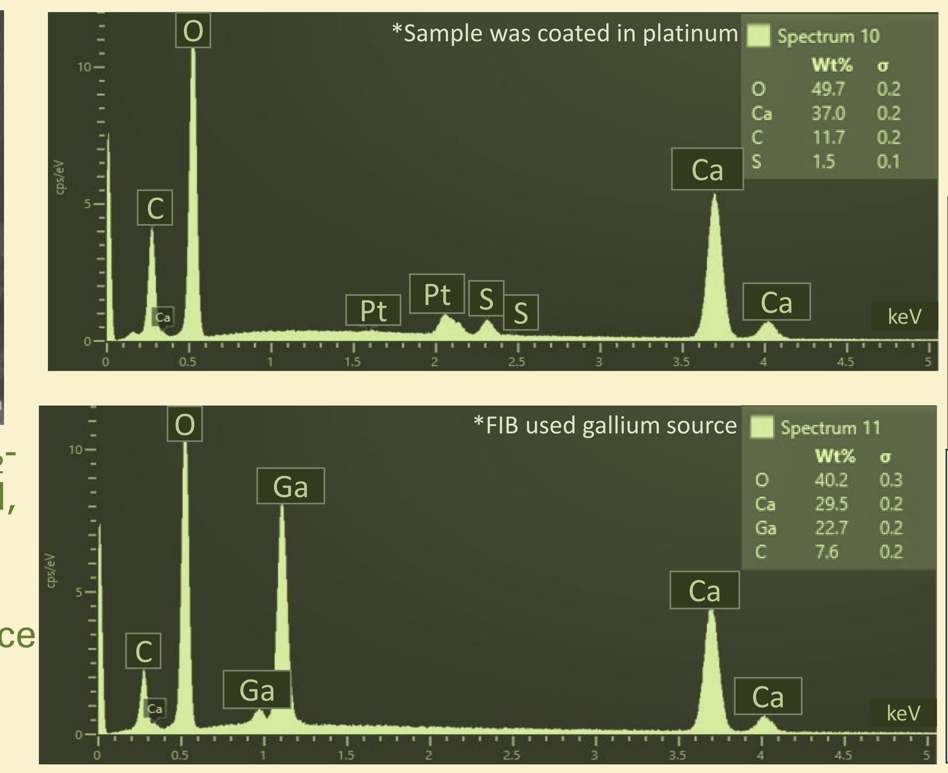
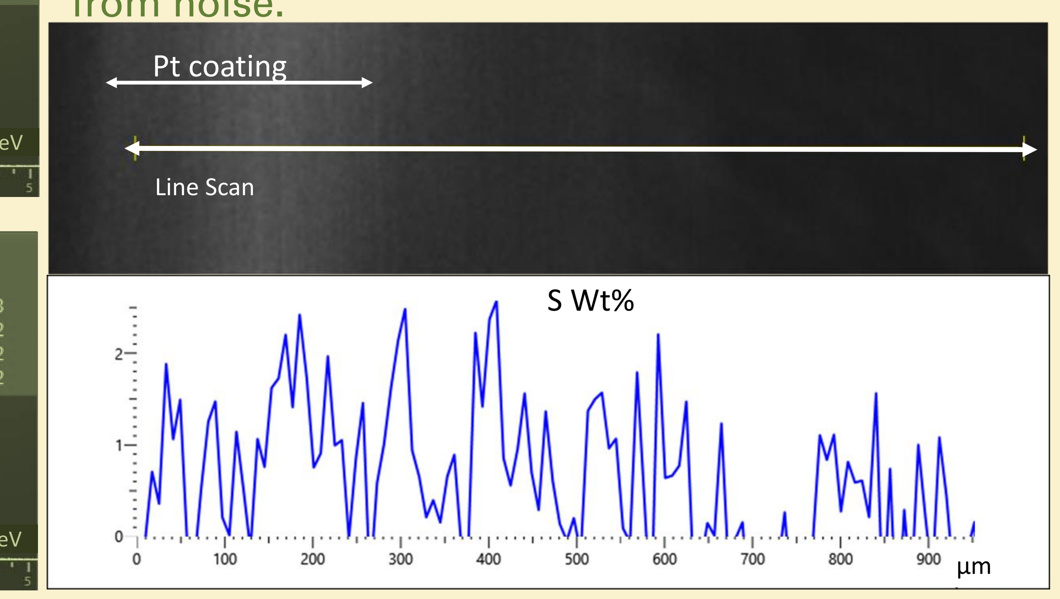


Figure 2: Calcite was heated to 460°C in CO_2-1.5% SO_2 for 5 days. The sample was milled, and EDS was used to determine the elemental composition at the surface (Spectrum 10) and 10 μm beneath the surface (Spectrum 11). The surface has trace amounts of sulfur compared to the subsurface (right).

Figure 3: After milling into the sample a line scan using EDS was performed on the cliff face (below). The sulfur abundance is barely distinguishable from noise.



700°C Experiment

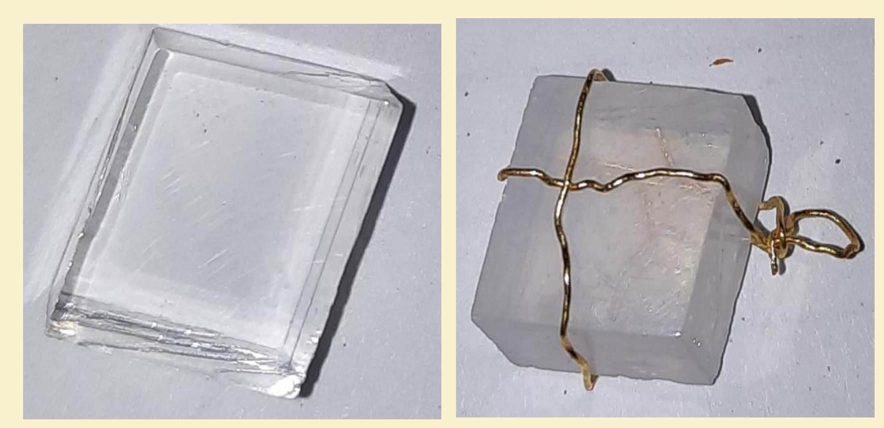


Figure 4: Calcite before (left) and after (right) it was heated to 700°C in CO_2-1.5% SO_2 for 5 days.

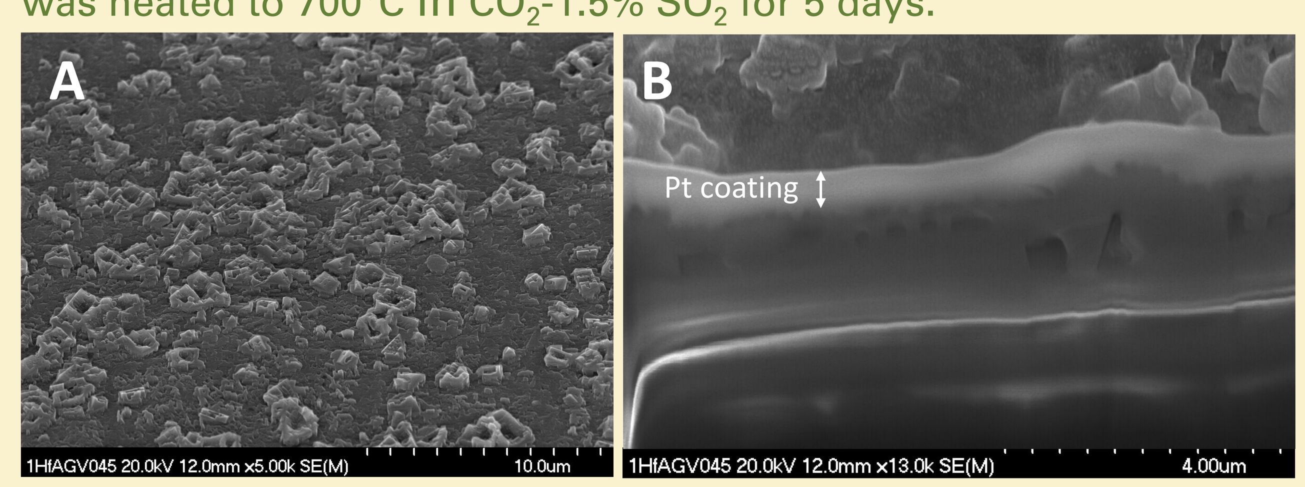


Figure 5: The surface of calcite after the experiment (A). The cliff face of the sample after it was milled via FIB (B). Void spaces are visible in the wall.

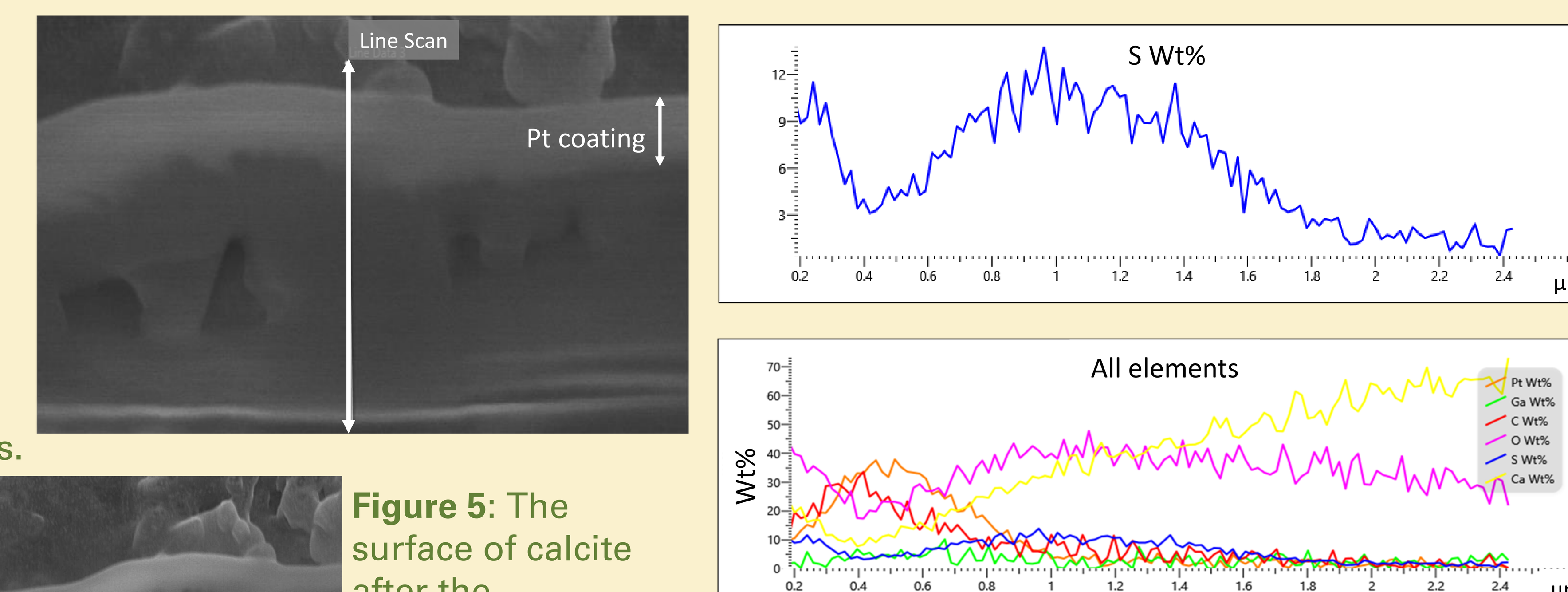


Figure 6: After milling into the sample a line scan using EDS was performed on the cliff face (above). Sulfur is concentrated at, and near, the surface of the sample (the dip at 0.4 μm is due to the platinum coating).

Next Steps

- Other calcium-bearing minerals will be investigated in the future (Table 1).
  - Each mineral was created under different formation processes and exhibit different crystal structures that will affect their interaction with SO_2
- Preliminary experiments will be completed for 1, 2, and 3 weeks
- Future analysis will include X-ray Photoelectron Spectroscopy (XPS) and potentially Transmission Electron Microscopy (TEM)

Mineral	Chemical Composition
Wollastonite	$CaSiO_3$
Grossular	$Ca_3Al_2(SiO_4)_3$
Anorthite	$CaAl_2Si_2O_8$
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$

Table 1: Future minerals that will be investigated during this research project.

Conclusions

- After calcite was heated to 460°C for 5 days, ~1 wt% of sulfur was detected on the surface
  - The surface did not exhibit new crystal growth
- When calcite was heated to 700°C for 5 days, up to 12 wt% of sulfur was detected at the surface
  - The entire surface was marked with new crystal growth
  - Voids were visible in the cliff face and were present up to a depth of 5 μm
  - Sulfur abundance decreased with depth
- More experiments for longer periods of time in both CO_2 and CO_2-1.5% SO_2 are necessary to determine the reaction rates

Acknowledgments

The PI was supported by an appointment to the NASA Postdoctoral Program at the NASA Glenn Research Center, administered by Universities Space Research Association under contract with NASA. The authors would like to acknowledge Nathan S. Jacobson (NASA Glenn), John Setlock (Univ. of Toledo/NASA Glenn), and Peter Bonacuse (NASA Glenn) for their assistance in the lab.

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